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A RADIOCHEMICAL STUDY OF ELECTROPLATING

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A RADIOCHEMICAL STUDY OF ELECTROPLATING

BY
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AND
GILBERT F. KINNEY

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A RADIOCHEMICAL STUDY OF ELECTROPLATING

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147
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TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
Introduction	1
Experimental	2
Results	4
Discussion	7
Tables	9
Appendix I	12
Appendix II	13
Appendix III	16
Literature Cited	17

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Title</u>	<u>Follows Page</u>
1	Diagram of the Circuit	3
2	Planchet Activity	6
3	Planchet Activity per Coulomb	6
4	Radiographs	7

ABSTRACT

The electroplating of silver from a radioactive solution onto a metal cathode was investigated to determine the suitability of the radioactive tracer technique for the study of irreversible electrode phenomena. It was found that when appropriate precautions are taken to assure a fixed specific activity of the plating bath and to mount reproducibly a sample in a counting chamber the radioactivity method is satisfactory for estimating the amount of plated material, if a flat surface or if a curved surface which can be flattened reproducibly is used. The statistical fluctuations appearing in the method are somewhat too large however to permit satisfactory measurements for precise quantitative studies of polarization phenomena, where small differences between large numbers are involved, at least with the techniques employed in this study. The same limitations also apply to methods based on radioautographs made from the radioactive plated material.

INTRODUCTION

Irreversible electrode processes are important in many practical situations such as the charge and discharge of a storage cell, in the electroplating of metals and in corrosion. These irreversible electrochemical processes are complex indeed when compared with conventional reversible electrode effects. It was the objective of this work to investigate the possible use of radioisotopes and tracer techniques in the study of these irreversible electrode processes. For this a simple electroplating problem was selected. The irreversibilities in this case are associated with a polarization phenomenon which gives rise to the so-called throwing power of the plating bath. In principle, the radiochemical methods offer a simple means of investigating directly various throwing power effects, and hence also of polarization and related irreversible phenomena.

The material selected for use in this study was radioactive Ag^{111} . This is a beta emitter, decaying with a half-life of 7.5 days, and emitting no gamma radiation. A conventional Geiger counter technique offers ample sensitivity for the measurement, and the short half-life, coupled with the lack of gamma emission, makes the safety and decontamination problems relatively simple. The radioisotope is readily incorporated into a conventional silver-plating bath, and standard plating techniques can be used for the preparation of the radio-active samples.

Theoretical Background. In the electrodeposition of a metal, an item of major importance is the current density and its distribution. This distribution depends primarily on electrode geometry and the associated electric field (1). Methods for the determination of the primary current density distribution as a result of electrode geometry have been described (2). But the actual current density distribution shows also a secondary dependence on the nature of the plating bath. This arises through an electrode polarization, which introduces a back electromotive force and a consequent distortion of the primary electric field. There results a

reduction in current from that which would be obtained if there were no such effect. This back EMF in general is greater at greater current densities; it is the distribution of these EMF and polarization effects that is the source of solution throwing power. This serves to diminish electrodeposits at locations of high current density, and provide relatively greater amounts at locations where low current density might be expected if the effects were only those of electrode geometry. It was hoped that the introduction of a radioisotope into the plating bath and adaptation of the tracer technique of measurement would permit some sort of quantitative study of these effects.

EXPERIMENTAL

Preparation of the Plating Bath. Neutron-irradiated palladium metal was obtained from the Oak Ridge National Laboratory. The samples, weighing about 3 g., contained about 5 millicuries of 7.5 day Ag^{111} , plus a large Pd^{109} activity, which latter, fortunately, had largely decayed out by time of arrival at the laboratory (13 hr. half-life). The mixture of metals was dissolved in aqua regia, inactive AgNO_3 was added as a carrier, and dilution sufficed to precipitate AgCl . The precipitate so obtained was generally orange in color, as a result of adsorbed palladium salts, and so it was found necessary to dissolve in aqueous ammonia and reprecipitate with HCl , yielding now a white solid. This latter, after being washed with dilute aqueous sodium nitrate, was dissolved in a $\text{KCN} - \text{K}_2\text{CO}_3 - \text{AgCN}$ solution to prepare an active stock solution, the final composition of which was 3.6% AgCN , 6% KCN , 4.5% K_2CO_3 (3).

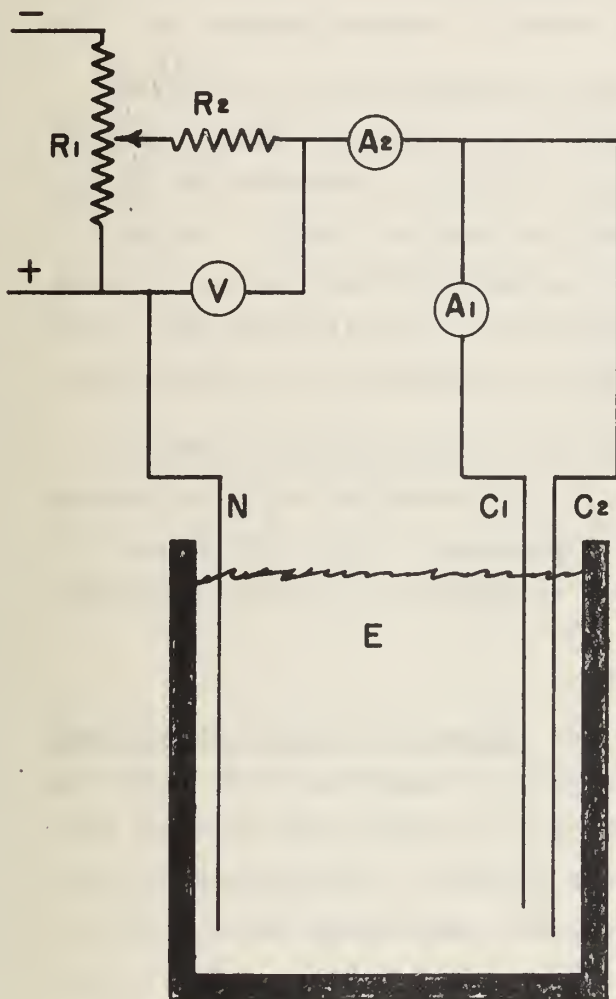
A portion of this radioactive stock solution was pipetted into sufficient inactive plating solution of the same composition to prepare 250 ml. total. The quantity of stock solution required depended on the age of the solution and on the desired activity of the final plating solution. Such a calculation is outlined in Appendix I.

The Electroplating Cell. Electrolysis was carried out in a cell constructed of polymethylmethacrylate, approximately $3\frac{1}{2}$ " x 2" inner dimensions, and holding about 250 ml. of solution. Grooves had been cut along the inside of the cell at various locations to position electrodes, and binding posts were attached to the outside to facilitate electrical connections.

The silver was plated onto planchets of the type ordinarily used in radiochemical work : thin copper discs of about $7/8$ " diameter. These were first cleaned thoroughly, including a bright dip and a cyanide dip, then plated with a thin coating of inactive silver (3). In most of the experiments the reverse side and the lead wires were protected with a stop-off compound. The planchet was mounted immediately in front of and was electrically in parallel with a cathode of silver foil, about 2" x 2", which thus covered one entire end of the cell. The anode was normally mounted at the other end of the cell about 3" away. For the circuit diagram, see Fig. 1. In earlier experiments a silver anode was used, but later it proved necessary to use an anode made of stainless steel. During all the runs the contents of the cell were stirred magnetically; all experiments were carried out at room temperature, approximately 25°C.

Power Source and Control. Direct current was supplied from storage batteries, and the current through the cell was controlled by a potentiometer circuit. Precision ammeters were arranged to read the current through the planchet and also the total plating current. By permitting the planchet current to flow through a short piece of Nichrome wire and measuring the resulting potential drop on a recording potentiometer, a visual trace of current versus time was also obtained.

The chart record was suitable as a precise timing device, and could also have been used to calculate the quantity of electricity as $\int i \, dt$. It was found, however, that manual control of the current gave sufficiently constant currents to permit merely multiplying current by time.



C_1 TEST PLANCHET

C_2 MASTER CATHODE

A_1 MILLIMETER FOR
TEST PLANCHET

A_2 AMMETER FOR TOTAL
CURRENT

V VOLTMETER

R_1 POTENTIOMETER FOR
CURRENT ADJUSTMENT

R_2 LOADING RESISTOR

E ELECTROPLATING BATH

N ANODE

FIG. 1. DIAGRAM OF THE CIRCUIT

Measuring Technique. Planchets were counted on a standard type Geiger-Müller counter with halogen-filled tube. The counter geometry, for the position used, was about 30%. About 10,000 counts were taken on each sample, so that the statistical counting error was no more than 1% (4).

The dead-time of the counter, estimated by the two-source method was about 0.1 millisec. Thus the coincidence correction, which has been applied to all data reported herein, amounts to $1/(1 - .0001m)$, where m is the measured number of counts per second of the sample.

The effect of self-absorption was estimated as follows: For the thickest sample used the total thickness of silver was about 5 mg/cm^2 , giving the effective thickness of approximately half this value, or 2.5 mg/cm^2 . Since the range of the 1 mev beta particles is about 400 mg/cm^2 , the maximum self-absorption error will be about $2.5/400$, or 0.6%. The value is less than the statistical counting error, hence no correction for self-absorption need be applied.

For the radiophotographs made, the planchets were placed in direct contact with the emulsion side of a metallographic plate (Eastman Kodak) for one to five days - depending on the activity of the sample - and developed from 3 to 5 minutes in a conventional high-contrast developer.

RESULTS

Experiments with Silver Anode. In a series of pilot experiments, strips of silver foil were used in front of the master cathode. A square cut from the strip was placed in the sample holder of the counter and its activity determined. It became apparent very soon, however, that because of the critical geometrical considerations of the counter, these squares could not be positioned with sufficient accuracy to obtain reproducible results. Hence provision was made to use circular planchets, as described above, which could be positioned accurately in the sample holder for counting.

In Table I are shown the results of a series of runs, using these circular planchets, all derived from the same plating solution (i.e., no additional radioactive stock solution was added during the course of the series.). The columns show A, the number of counts per second on the planchet, corrected for dead-time; T, the time, in days, measured from datum zero (the beginning of the first run) to the time of counting the sample; t, the duration of the run, in seconds; I, the total plating current. All these runs were performed at a constant planchet current of 25 ma. B_0 is a computed value of the number of counts per second per coulomb, corrected for radioactive decay since $T = 0$ and for depletion of radioactive silver in the plating bath (since it is being constantly replaced by inactive silver from the anode). Details of computing B_0 are given in Appendix II.

It was expected that B_0 should have remained constant throughout the series of runs, but an examination of Table I shows clearly that the value decreases appreciably, even during the runs of a single day, and very markedly after a week.

Two possible sources of difficulty were examined: (a) drag-out (due to solution adhering to the planchet when removed) and (b) exchange between inactive silver on the planchet with active in the solution; either of these would tend to decrease the amount of active silver remaining in solution. By actually weighing a planchet before and after dipping into an inactive plating solution, the drag-out error was found to amount to about 0.03% per planchet. Planchets placed into active plating solution for as long as 24 hours showed no appreciable exchange in these circumstances - i.e., planchet activity was not detectable over counter background. Thus neither of these effects can explain the observed results.

It is believed that this apparently anomalous drop in B_0 is caused by an increase in the inactive silver concentration - not accounted for in the calculation of B_0 - by air oxidation of the silver electrodes:



Now the planchet current measures only the total amount of silver deposited per unit time; and thus if the ratio of inactive to active silver is too large, the observed radioactivity of the planchet will be too low, as was found.

Experiments with Stainless-Steel Anode. To eliminate the error referred to at the end of the previous section, a stainless-steel anode was employed for the remaining runs. During the day's operation, cathode current was left on continuously, thus to protect the cathode from air oxidation; planchet current was started and stopped by connecting or removing from the solution. The cathode was rinsed and removed from the plating bath when not in use. With this arrangement it was no longer necessary to correct for depletion of active silver, since active and inactive were used up at the same rate; i.e., the specific activity remained constant.

In Table II are shown the results of a series of runs performed in this fashion, all at a planchet current of 25 ma. and from a single initial plating solution; this series will be referred to as Series I. A is the counting rate of the planchet, in counts per second; T, the time in days elapsed from datum zero until the planchet was counted; t, the duration of the run in seconds; C/it the ratio of the number of counts per second, corrected for decay to T = 0, to the quantity of electricity passing through the planchet. Table III gives results from a second plating solution, Series II. The first half of the table is for planchets run at 25 ma. planchet current; the second half, all for 300 sec., but at varying currents. The starred value in Table III is for a planchet which had been bent, prior to plating, such that the two halves formed a 45° angle with the cathode, the vertex of the bend running vertical. This planchet was then flattened before counting. Within each series C/it should be constant, though not from one series to another.

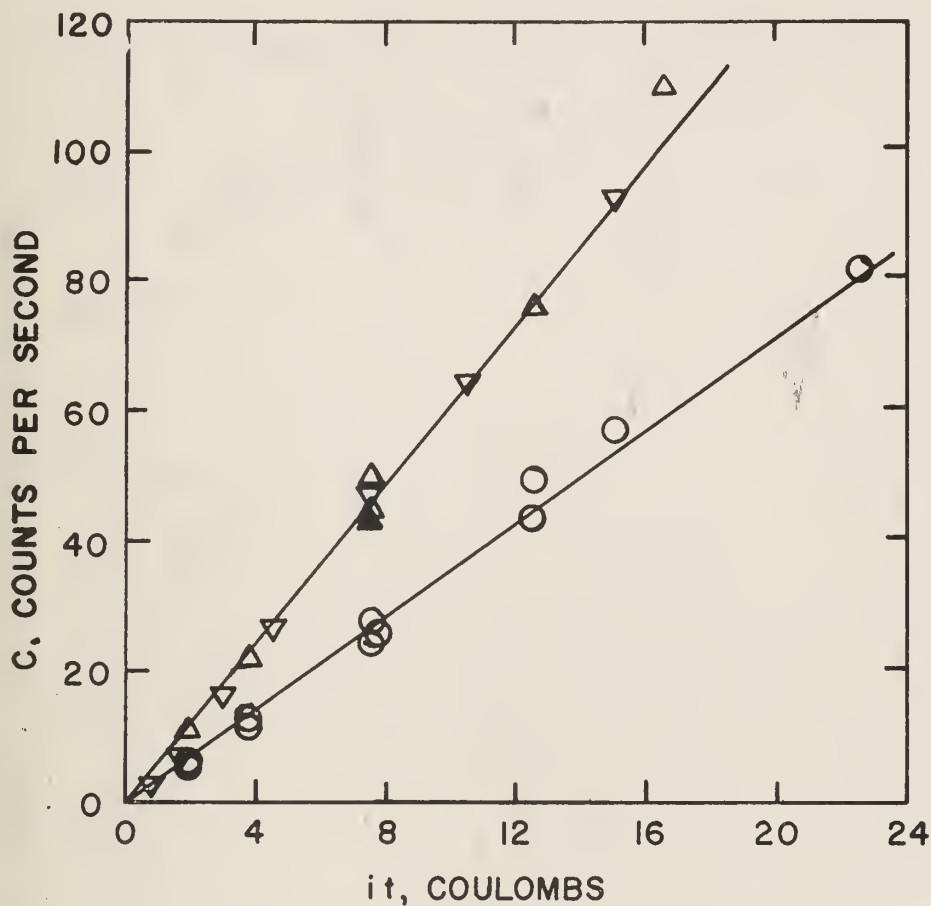


FIG. 2, PLANCHET ACTIVITY

SERIES 1, VARIABLE t , CIRCLES

SERIES 2, TRIANGLES

VARIABLE t , UPRIGHT TRIANGLES

VARIABLE i , INVERTED TRIANGLES

BENT PLANCHET, SOLID TRIANGLE

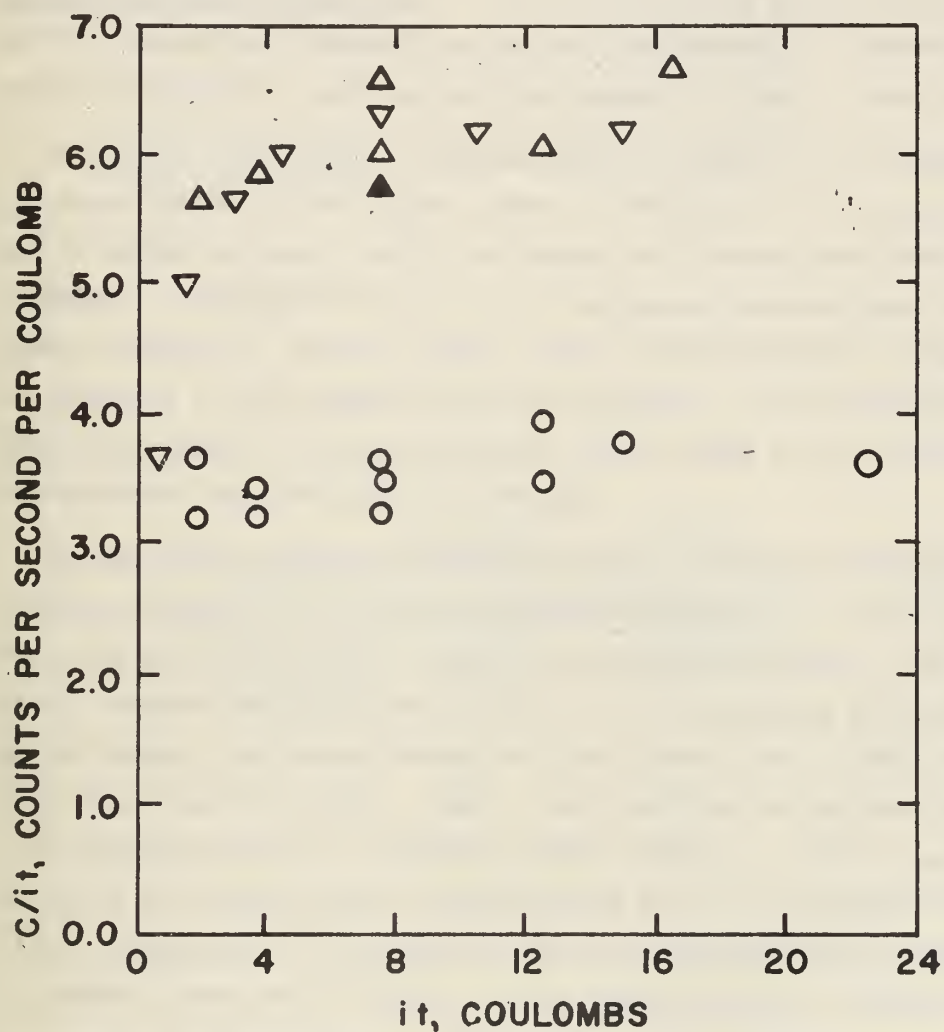


FIG. 3, PLANCHET ACTIVITY PER COULOMB

SERIES 1, VARIABLE t , CIRCLES

SERIES 2, TRIANGLES

VARIABLE t , UPRIGHT TRIANGLES

VARIABLE i , INVERTED TRIANGLES

BENT PLANCHET, SOLID TRIANGLE

In Fig. 2 are plotted C , the planchet activity corrected for decay against it, the quantity of electricity passing through the planchet; in Fig. 3, C/it vs it, thus emphasizing the lack of precision.

The Photographic Technique. It was considered possible that certain of the limitations imposed by the critical nature of counter geometry could be avoided by making radiophotographs of the plated material.

In Figure 4 are shown reproductions of some of the radiographs made. The upper third of the figure shows a radiograph of the entire cathode for a rather critical case: the anode and cathode were very close together - separated by only a 1/4" polymethylmethacrylate rod. Under these conditions, current density (and thus thickness of deposit) should be expected to vary widely along the surface of the electrode; but the radiograph shows no such variation, there being only a blank area where the electrode was shielded by the rod.

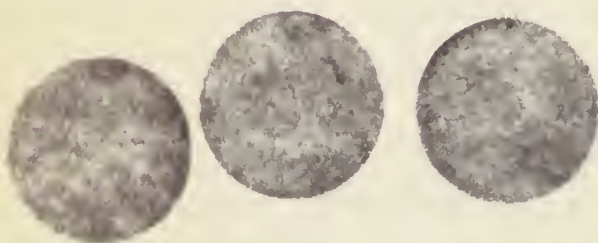
In the middle and lower third of Fig. 4 are shown radiographs of several planchets, all at the standard distance of 3" from the anode, but none protected on the reverse by stop-off compound. Of these, the first, fourth, and sixth radiographs are of planchets placed perpendicular to the anode; the second shows the face toward the anode; and the third, that away from the anode. Again, the expected variations in activity with position were not observed; there appears, in fact, to be as much activity (as shown thus) on the reverse as on the observe side. The fifth radiograph of this series shows the uneven deposit obtained from a planchet improperly cleaned. This unevenness was, however, quite as obvious to the naked eye as it is in the photograph.

DISCUSSION

Tables II and III and Fig. 2 show an approximate linearity of C with it for the experiments using the stainless-steel anode. Fig. 3, on the other hand, shows clearly that the random errors are quite significant -



II.



c

a

b

III



c

d

c

III

an average deviation of perhaps 5% is shown. The bent planchet of Series II (the solid triangle) falls within this random error - but this was the only successful case of a number of attempts to flatten a previously bent planchet such that it could be reproducibly counted.

It should be noted that at the very low currents used in some of the runs of Series II, C/i is much less than anticipated. No explanation is apparent for this phenomenon, for it is to be expected that side reactions (such as hydrogen formation) which would tend to reduce the plating efficiency would be of more importance at high rather than at low current densities.

The counting technique can be used to estimate - within the limits of error noted above - the thickness of electroplated material (which is proportional to the measured activity) for flat specimens or for specimens that can be flattened reproducibly. The latter-mentioned case suggests the rather powerful use for studying electroplating on surfaces of irregular shapes, where theoretical predictions (2) as to current density are impossible. However, some sure methods must be found to flatten planchets with sufficient reproducibility to insure conformity with counter geometry. Even for flat planchets the method cannot be recommended without reservation, since considerable advance preparation is necessary for experiments of this type, and the ultimate rapidity of the determinations manifests itself only if a large number is required, or if no other method appears feasible. Furthermore, for investigation of polarization phenomena, where small differences must be examined, the statistical fluctuations inherent in the method of this paper introduce quite large errors.

Results obtained from the radiographic technique confirm the general observation that photographic detection, suitable for qualitative work has inherent difficulties when applied to the quantitative determination of small differences in large amounts.

TABLE I. RUNS WITH SILVER ANODE i = 25 ma.

<u>A, c/sec.</u>	<u>T, days</u>	<u>t, sec.</u>	<u>I, ma.</u>	<u>B₀, c/sec./coulomb</u>
37.4	0.042	298	240	5.22
76.0	0.104	590	215	5.43
6.75	0.138	60	220	4.92
13.8	0.167	119	220	5.08
17.2	0.188	150	215	4.75
106.6	0.198	875	205	5.15
49.3	5.932	905	250	4.22
95.3	6.025	1846	220	4.17
58.0	6.125	1200	185	4.24
139.9	6.135	300	172	4.20
28.9	6.156	606	168	4.37
7.57	6.167	180	164	3.89
10.2	6.188	240	162	4.05
4.98	6.208	121	161	3.88
2.24	6.958	61	162	3.78

TABLE II. RUNS WITH STAINLESS-STEEL ANODE

SERIES I. $i = 25$ ma.

<u>A, c./sec</u>	<u>T, days</u>	<u>t, sec</u>	<u>C/it,c/sec./coulomb</u>
56.7	0.010	600	3.78
27.3	0.017	300	3.65
12.9	0.027	150	3.44
6.85	0.038	75	3.67
44.0	0.066	450	3.94
20.3	11.06	600	3.77
29.4	11.08	900	3.63
6.57	14.05	300	3.23
3.82	15.69	150	3.21
10.6	14.07	450	3.48
6.55	15.05	305	3.49
1.49	14.99	75	3.20

TABLE III. RUNS WITH STAINLESS-STEEL ANODESERIES II

<u>A, c/sec</u>	<u>T, days</u>	<u>t, sec</u>	<u>i, ma</u>	<u>C/it, c/sec/coul.</u>
49.2	0.00	300	25	6.56
45.1	0.01	300	25	5.99
109.9	0.01	660	25	6.65
43.8	0.02	300	25	5.87
67.7	0.03	450	25	6.04
10.5	0.03	75	25	5.63
21.6	0.05	150	25	5.82
42.6*	0.06	300	25	5.72
2.32	1.92	300	2.5	3.68
6.25	2.00	300	5.0	5.01
14.1	2.04	300	10.0	5.65
22.3	2.06	300	15	6.02
39.1	2:07	300	25	6.31
53.3	2.08	300	35	6.17
76.4	2.09	300	50	6.18

* Bent planchet

APPENDIX I

Quantity of Active Stock Solution to be Added to Inactive Plating Solution

Let A be the number of counts per second desired on the planchet, resulting from a current, i , passing through the planchet for t seconds. Then the total number of gram-atoms of silver electroplated onto the planchet will be given by $it/96,500$. If the volume of the plating solution is V_1 , the density d , and the percentage of AgCN in the bath $100p$, the total number of gram-atoms of silver in the bath will be $pV_1d/134$ (where 134 is the formula mass of AgCN). Then the fraction of silver that is plated onto the planchet is,

$$f = 134it/96500 p V_1 d.$$

Now, assuming an overall counting efficiency of e , there must be sufficient activity on the planchet to produce Ae disintegrations per second, or, the number of millicuries on the planchet must be $Ae/(3.7 \times 10^4)$. And thus the number of millicuries in solution at that time, M , must be

$$M = \frac{Ae}{3.7 \times 10^4} \times \frac{1}{f},$$

since for each millicurie in solution, only f millicuries will be plated onto the planchet.

Assume now that T days have elapsed since m millicuries of Ag^{111} were added to the active stock solution, of volume V_2 . Then in the stock solution at any time the number of millicuries present is me^{-kT} , k being the decay constant, equal to $\ln 2 / 7.5$ for Ag^{111} , T in days. And thus v , the volume of stock solution to be added, is given by the expression

$$v = V_2 \times \frac{M}{me^{-kT}}.$$

APPENDIX II

Correction for Depletion and Decay, for Experiments with the Silver Anode

Let a be the molar concentration of all silver in the plating bath. It is here assumed that a remains constant, since silver is replaced from the anode at the same rate as it is plated out at the cathode, or $da/dt = 0$. At any given instant, however, the rate at which silver is plated onto all cathode surfaces will be given by I/F , where I is the total cathode current, F , the Faraday constant. If we let c be the number of counts per second in the plating bath, then the rate of depletion of active silver will be in proportion to the specific activity of the solution, which is measured by c/aV , the number of counts per second per gram-atom of total silver. And thus it follows that

$$\frac{dc}{dt} = -\frac{c}{aV} \times \frac{I}{F},$$

or, integrating, $c = c_0 e^{-Q/aVF}$, where $Q = \int_0^\Theta Idt$, Θ being the total elapsed time for running the cell, and c_0 being the number of counts per second present in the cell when $\Theta = 0$. Now $dq = Idt$, and thus

$$dc = -\frac{c_0 I}{aVF} e^{-Q/aVF} .dt.$$

Let A be the number of counts per second on the planchet. The rate at which activity is plated onto the planchet is proportional to the rate of loss from solution, multiplied by the ratio of planchet current, i , to the total current, or

$$dA = -\frac{i}{I} dc = \frac{c_0 i}{aVF} e^{-Q/aVF} dt.$$

We shall wish to integrate this over the duration of a given run; for this period, Q may be considered effectively constant, and when $t = 0$, $A = 0$. Hence, letting t be the duration of the run, $q = \int_0^t idt$,

$$A = \frac{c_0 q}{aVF} e^{-Q/aVF}.$$

Now let b represent the number of counts per second per coulomb on the planchet.

$$b = \frac{A}{q} = \frac{c_0}{aVF} e^{-Q/aVF}$$

In order to correct for depletion, then, we shall wish to calculate B , the value b would have at $Q = 0$. From the preceding,

$$B = \frac{c_0}{aVF} = be^{Q/aVF}.$$

It now only remains to correct B for the decay of the Ag^{111} . Letting B_0 be the value of B corrected also for decay,

$$B = B_0 e^{-kT},$$

in which k is the decay constant, $\ln 2 / 7.5$, and T the time in days elapsed since datum zero. Hence

$$B_0 = Be^{kt} = be^{Q/aVF} e^{kT}$$

or

$$B_0 = \frac{A}{q} e^{(Q/aVF + kT)}$$

The symbols in the last equation are redefined as follows:

B_0 , counts per second per coulomb, corrected for depletion and decay.

A, counts per second on the planchet

q, number of coulombs passing through planchet for the run

Q, total number of coulombs passed through the cell since datum zero

aV, number of gram-atoms of total silver in the plating bath

F, the Faraday constant, 96500 coulombs per gram-equivalent

k, the decay constant of Ag^{111} = 0.0924 day^{-1}

T, time in days since datum zero

APPENDIX III

Sample Reduction of Data

The run chosen for illustration is the last one of Series II (Table III). Datum zero for Series II was 1420 hours on 4 June 1956. This planchet was run at 50.0 ma. for 300 sec., and registered 178 counts, on a scale of 128, in 300 sec., when counted at 1630 hours on 6 June. The background of the counter was previously determined to be 0.2 counts (scale of 128) per 100 sec. Thus, in these units, the counting rate was $178/3.00 - 0.2 = 59.1$, in counts (scale 128) per 100 sec. To convert to actual counts per second, this value must be multiplied by 1.28, leading to the observed counting rate, $m = 75.7$ counts/sec. This must then be corrected for the dead time of the counter (1×10^{-4} sec.). If A is the activity, corrected for deadtime,

$$A = \frac{m}{1 - .0001m} = \frac{75.7}{1 - .008} = 76.4 \text{ counts/sec.}$$

Two days, two hours, ten minutes have elapsed since datum zero, or $T = 2.09$ days. Thus the activity corrected for decay, $C = Ae^{kT}$, where $k = .693/7.5 = 0.0924 \text{ day}^{-1}$, and thus $C = 76.4 e^{.0924 \times 2.09} = 92.8$ counts/sec.

The quantity of electricity, $it = 0.0500 \times 300 = 15.0$ coulombs. And thus $C/it = 92.8/15.0 = 6.18$ counts per second per coulomb.

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